

Separation and recovery of nickel, as a salt, from an EDTA leachate of spent hydrodesulphurization catalyst using precipitation methods

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HIGHLIGHTS

- Recycling of Ni from an EDTA leaching solution of a spent HDS catalyst.
- Precipitation of EDTA in acidic medium in two stages.
- Separation of Al and Mo by precipitation.
- Fe replacement and recovery of 93% Ni, as $\text{Ni}_3(\text{PO}_4)_2$, purity $\geq 96\%$.
- Nearly closed environmental-friendly cycle.

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ABSTRACT

The aim of the present work was to recover Ni, as a salt, from an ethylenediaminetetracetic acid (EDTA) solution that also contains Al and Mo, obtained after leaching a spent Ni–Mo hydrodesulphurization catalyst.

The pH for EDTA precipitation was optimized in order to maximize further separation of Al and Mo from Ni. At pH = 1, 80% of EDTA was precipitated, followed by precipitation of Al and Mo (recovery of 94 and 67%, respectively) at pH 5. From this point, three options for recovering Ni, as a salt, were studied. The first consisted on a second EDTA precipitation at lower pH followed by Ni precipitation, as $\text{Ni}(\text{OH})_2$, by increasing the pH; the second and the third ones involved sequential addition of Fe^{3+} and phosphate ions, with and without the second EDTA precipitation step, respectively. The addition of Fe induces the substitution of Ni in the EDTA complexes, leaving Ni free to precipitate with the phosphate, which maximizes Ni recovery.

The highest Ni recovery was 93%, as nickel phosphate, with a purity $\geq 96\%$ in the sequence involving second EDTA precipitation, where 70% of the remaining EDTA was recovered at pH 0.4, followed by addition of Fe^{3+} and precipitation as nickel phosphate. However, this option has the highest costs in terms of reagents consumption. By suppressing the second EDTA precipitation step, nickel phosphate was recovered with lower yield and purity (82 and 94%, respectively). In the case, where Ni was precipitated as $\text{Ni}(\text{OH})_2$, nickel recovery only reached 70%, with $\geq 97\%$ purity; still, this possibility has the lowest reagents cost. In the two options that included phosphate addition, the analysis of the obtained solid suggests the $\text{Ni}_3(\text{PO}_4)_2$ stoichiometry and the proposed process is clean, with almost no generation of residues, since the precipitated EDTA can be recycled into the leaching stage and the Fe, recovered as a solid, can be reused as an iron source.

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1. Introduction

Spent hydrodesulphurization (HDS) catalysts are hazardous residues produced in large quantities in petroleum refining industries (Dufresne, 2007; Rapaport, 2000). The recovery of the valuable metals, like molybdenum (Mo), nickel (Ni), vanadium (V) and cobalt (Co), present in such catalysts, which are usually alumina-based, has been

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object of extensive study in order to find inexpensive, efficient and environmentally friendly processes (Zeng and Cheng, 2010). Hydro-metallurgical processes have the advantage of using lower temperatures and allow better control on the recovery of by-products when compared to pyrometallurgical ones; however, some reagents are expensive, the reaction rates are much slower and large quantities of concentrated solutions are required (Ghosh and Ray, 1991; Kim et al., 2009). The leaching of metals from spent HDS catalysts is commonly accomplished using concentrated acid solutions, such as sulfuric acid, which allows almost complete solubilization of all the metals present in the catalyst (Idris et al., 2010; Kim et al., 2009; Valverde et al., 2008). This procedure leads to succeeding separation stages, usually based on

the combination of solvent extraction and precipitation steps. When the goal is to recover Ni or Co from an Al solution, several studies can be found, most of them based on solvent extraction (Kim and Cho, 1997; Park et al., 2012, 2007; Rao et al., 2012; Zhang et al., 1995). Orive et al. (1992) compared a process of direct precipitation, where Ni and Co precipitated at $\text{pH} > 12.5$, with solvent extraction of Al, using Cyanex 272 or LIX 26 as extractants. Extraction using Cyanex 272 proved to be more effective than precipitation, as the second led to a solid of Ni and Co with significant amount of Al. Precipitation of Al at pH around 5 is efficient; however, some Ni is usually lost to the solid so this method is only advisable if Ni is in great excess (Lee et al., 2010). Valverde et al. (2008) proposed a method based on the precipitation of Ni and Co as oxalates while the complex of Al-oxalate remains soluble. In general, the methods found in the literature to separate Ni from an excess of Al are based on solvent extraction because simpler inexpensive methods, like precipitation, are not efficient in terms of separation.

Alternatively, leaching processes can be performed using an organic acid such as ethylenediaminetetracetic acid (EDTA), that leads to a more selective dissolution of Ni/Co from an alumina-based catalyst (Pinto and Soares, 2013a). Some Al and little Mo are also solubilized and separation of metals, as well as EDTA, must be performed. To recover metals from solution, where they are complexed with EDTA, EDTA is usually precipitated in very acidic conditions leaving the metals free to be recovered (Goel et al., 2009). However, if complexes are still stable in such conditions, EDTA precipitation is not complete and metal complexes remain. Electrochemical processes and replacement reactions are possibilities to recover metals from EDTA solutions.

The deposition of Ni in the presence of EDTA by electrochemical membrane processes has been tried; however, results present in the literature have discrepancies: Juang and Wang (2000) stated that no deposition of Ni was observed in the wide pH range studied and at high current density; Otzekin and Yazicigil (2006) presented results that indicate the possibility of recovering Ni by electrolysis, in the presence of EDTA, in a two-chamber cell.

The replacement reaction consists on substituting the metal in the complex by another one in order to precipitate the one intended to recover. In the case of EDTA, this is usually done by iron replacement, which forms very stable complexes that can be recovered latter by precipitation in alkaline conditions. This method has been applied to soil washing solutions: Di Palma et al. (2003) recovered Cu and Pb from an EDTA solution by studying both phosphate and hydroxide precipitation; Lo and Zhang (2005) recovered Pb and Zn by addition of phosphate after Fe replacement; Lim et al. (2005) precipitated Pb, Cd and Ni in their phosphate forms from spent EDTA solutions.

The aim of this work was to separate and recover Ni, as a salt, from a leaching solution of spent HDS catalyst. Leaching was performed with an EDTA solution; therefore, the leachate contains EDTA in excess, as well as Al and some small amount of Mo. Methods based on precipitation were studied and discussed and a final nearly-closed process is proposed.

2. Experimental

2.1. Leaching of spent HDS catalyst

The aqueous solution, used in this work, was obtained by leaching of a spent Ni–Mo HDS catalyst, using an EDTA solution. This leaching stage was studied as the second stage of a process for selective dissolution of metals from a spent Ni–Mo catalyst. Briefly, the first leaching stage was performed according to previous optimized conditions (Pinto and Soares, 2012): catalyst was roasted (500 °C, 90 min) and leached using microwave-assisted method (NaOH 10 g/L, S/L=50 g/L, 4 heating cycles of 30 s each). The catalyst was

Table 1

Metal concentrations of the initial solution, obtained by leaching a spent HDS catalyst with 0.1 M EDTA.

Metal	Ni	Al	Mo
Conc., mol/L	1.98×10^{-2}	1.97×10^{-2}	1.20×10^{-3}

separated from the leachate by filtration and dried at 105 °C for 12 h in order to standardize weight before the second leaching stage.

The second leaching stage was accomplished with 0.1 M solution of EDTA and using microwave heating (pH=10.8, S/L=50 g/L, 4 heating cycles of 60 s each) (Pinto and Soares, 2013a). After four cycles, the solid and liquid phases were separated by filtration and the leachate was used to perform the precipitation studies. The metal concentrations in the obtained solution are presented in Table 1.

2.2. Computer chemical simulations

Species distribution diagrams were constructed based on chemical speciation calculations that were executed using MINEQL+ Version 4.5 (Schecher and McAvoy, 2003). Chemical equilibrium concentrations of all species considered in the model by the program reactions were generated based on the component stability constants (Martell and Smith, 2004) and the molar concentrations (Table 1).

2.3. EDTA precipitation

EDTA precipitation was accomplished by lowering the pH through the addition of concentrated HNO_3 . Studies were performed using 20 mL of the respective solution and after acid addition the flasks with the solutions were left agitating at room temperature to achieve equilibrium. Different pH ranges were tested depending if the EDTA precipitation was performed before or after Al and Mo precipitation; in the first EDTA precipitation, the pH was varied between 0.1 and 2.5 and duration went from 3 to 24 h; in the second EDTA precipitation, the pH range studied was between 0 and 0.5 with duration of the experiment of 3–4 days. The solids were then separated by centrifugation (2500 g, 10 min), washed with deionized water and dried at 105 °C until a constant weight was reached. Rigorous amounts of the solid were weighted and dissolved in NaOH (0.1 M) and the volume was made up to 50 mL for analysis.

2.4. Al and Mo precipitation

After first precipitation of EDTA, the pH was increased by the addition of NaOH to values between 3 and 10 and experiments were left for 1 h before separating the solid by centrifugation. Similarly to EDTA, the solid was washed and dried; then, rigorous weighted samples were dissolved in aqua-regia and heated in a water bath for 2 h. After complete dissolution, the solution was transferred to a volumetric flask and volume was made up to 50 mL.

2.5. Nickel replacement and its recovery as salts

Nickel hydroxide was recovered by increasing the pH of the respective solution to values higher than 9, by the addition of NaOH.

To study the precipitation as nickel phosphate, instead of hydroxide, an approach where Ni ion was replaced by Fe^{3+} ion was studied. Solutions of Fe and phosphate were prepared. A Fe solution (0.4 M) was prepared from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ was used to prepare a 1 M phosphate solution. A rigorously measured volume of Fe was added to the Ni–EDTA solutions and left under

constant agitation for 1 day to reach the equilibrium; so, Fe replaces Ni in the EDTA complexes. Then, immediately after addition of phosphate solution, concentrated NaOH solution was used to increase the pH (between 7 and 11.5). The system was filtered to separate the solid from the liquid. The time between phosphate addition and filtration was varied from 30 s to 20 min. The solid was washed with deionized water, dried and dissolved in nitric acid for analysis.

2.6. Analytical methods

Concentrations of EDTA, Ni, Al and Mo in the supernatant and in the dissolved solids were determined and mass balances were confirmed for each one.

Ni, Al and Mo were determined by atomic absorption spectroscopy with flame atomization (AAS-FA) with a Perkin-Elmer AAnalyst 400 spectrometer (Norwalk, CT, USA) using an air–acetylene (Ni) or nitrous oxide–acetylene (Al, Mo) flame.

EDTA concentrations were calculated from total organic carbon determinations using a Shimadzu TOC-5000A analyzer (Kyoto, Japan).

Phosphorus concentration was determined by spectrophotometry at 880 nm, after reaction with molybdate (sulfuric acid + potassium antimonyl tartarate + ammonium molybdate + ascorbic acid) (US EPA, 1978), using a Genesys 10UV Scanning spectrophotometer (Thermo Scientific).

3. Results and discussion

The sequential process flow sheet, showing the several steps implemented in this work to recovery Ni and EDTA from the EDTA

solution originated from leaching a spent HDS Ni–Mo catalyst, is shown in Fig. 1.

3.1. EDTA precipitation

Leaching of spent HDS Ni–Mo catalyst with a 0.1 M solution of EDTA led to a solution containing 1.16 g/L of Ni, 0.532 g/L of Al and 0.115 g/L of Mo (molar concentrations in Table 1). It is known that EDTA precipitates at low pH as H_4EDTA ; this method is commonly used to recover this compound from aqueous solutions (Di Palma et al., 2003; Goel et al., 2009). However, complexed EDTA might be harder to precipitate, depending on the solubility and stability of the complexes. Computer simulations were performed, considering the molar concentrations of EDTA, Ni, Al and Mo in the solution obtained after leaching. The percentage of EDTA, which is predicted to be uncomplexed, is represented in Fig. 2 (continuous line). Above pH 1.5, Ni, Al and Mo are all in the form of complexes while 60% of the total EDTA is free, which corresponds to the excess of EDTA relatively to the metals. Below pH 1.5, Mo starts to be uncomplexed, followed by Al. At pH 0.75, both metals are free, leaving 80% of EDTA uncomplexed while the remaining 20% are present as Ni–EDTA complexes. Below pH 0.5, even Ni complexes, that are more stable, start to break, but free EDTA never reaches 100% for $pH > 0$.

Experiments were performed to quantify EDTA precipitation at different pH values. After the addition of HNO_3 , the flasks were left for 24 h to achieve equilibrium. The experimental points (Fig. 2) show that EDTA recovery from the leaching solution was close to the theoretical predictions for uncomplexed EDTA present in solution (continuous line). As expected, the recovery of EDTA increased with the decrease of pH because the metals begin to be in the free form leaving EDTA available to precipitate. Maximum recovery of EDTA was

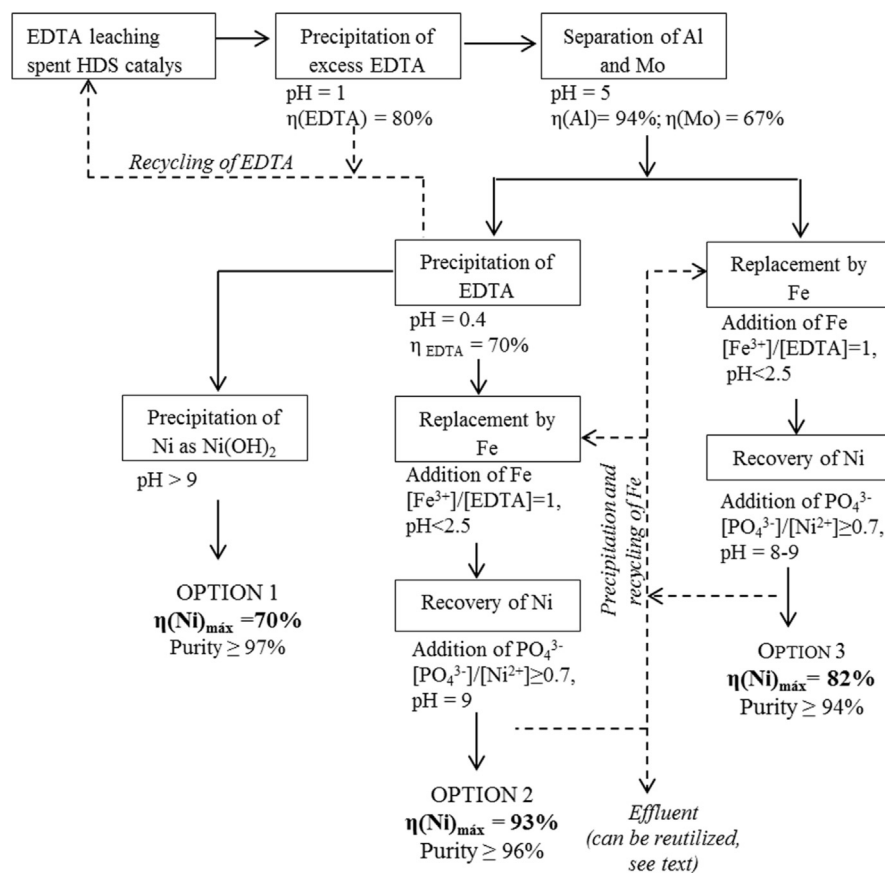


Fig. 1. Flow sheet of the processes developed for recovering Ni from an EDTA solution originated from leaching a spent HDS Ni–Mo catalyst.

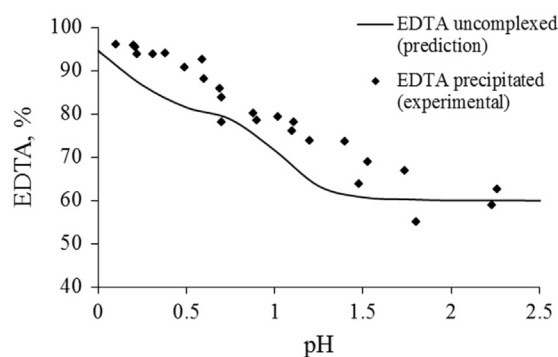


Fig. 2. Variation of EDTA precipitation with the pH from an initial solution containing 2.0×10^{-2} , 1.9×10^{-2} , 1.2×10^{-3} and 0.1 M of Ni, Al, Mo and EDTA, respectively. Each point represents a single experiment.

obtained in the pH range between 0.4 and 0 with a value of 95%. According to the chemical speciation simulations (Fig. 3A), the remaining EDTA was still complexed with Ni as NiH_xEDTA species. Using a pH below 0.4, we obtained a good recovery of EDTA, whilst metals remain in the aqueous solution, which was verified by AAS-FA measurements. The solid of EDTA had high purity with a maximum content of metals of 0.05 wt% of Ni, 0.1 wt% of Al and 0.2 wt% of Mo. Measurements of TOC confirmed that the content of H_4EDTA in the solid was $99 \pm 4\%$.

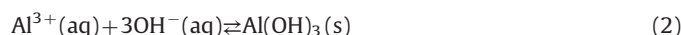
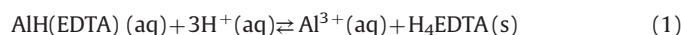
Experiments with duration of 3 and 6 h were tested and results did not differ significantly from the ones obtained after 24 h; hence, it is possible to conclude that after 3 h dechelation had occurred.

3.2. Separation of Al and Mo

Al is highly insoluble in aqueous solutions between pH 4 and 11 due to the formation of $\text{Al}(\text{OH})_3$, while Ni only starts to precipitate at pH above 7. However, the separation of these two metals is usually done by solvent extraction (Kim and Cho, 1997; Park et al., 2012; Rao et al., 2012) because the increase of pH to values between 4 and 5, to precipitate $\text{Al}(\text{OH})_3$, also leads to co-precipitation of Ni (Lee et al., 2010), which was verified experimentally. Similarly, Mo, that is soluble in this pH range, tends to precipitate together with Al (Pinto and Soares 2013b), which is an advantage in this case because it increases the purity of Ni solution.

As suggested by computer simulations (Fig. 3), Al complexes are broken before Ni ones and the results for EDTA precipitation seem to indicate the same. So, to avoid the use of an organic extraction process, the presence of EDTA itself was used to study a separation of Al from Ni, based on different stability of the complexes in acidic medium. This way, during the EDTA precipitation (studied in Section 3.1), instead of aiming for higher EDTA recovery, the goal was to obtain a good separation of Al and Ni.

After precipitation and recovery of EDTA, as a solid, the pH of the remaining solution was increased to 5.5 in order to study precipitation of Al. Fig. 4 shows the variation of precipitation of Ni, Al and Mo taking into account the pH of the first stage (EDTA precipitation, Section 3.1). When pH was reduced to values around 1.5 the complexation between EDTA and Al begins to decrease and EDTA starts to precipitate (Eq. (1) and Fig. 2); a similar situation happens with Mo. Because Al^{3+} is in the free form, when the pH is increased to 5.5, it precipitates as hydroxide (Eq. (2))



In the case of Ni, for pH below 1.5, $\text{NiH}(\text{EDTA})$ species is protonated into $\text{NiH}_2(\text{EDTA})$ (Fig. 3A) and only for pH below 0.8, this complex

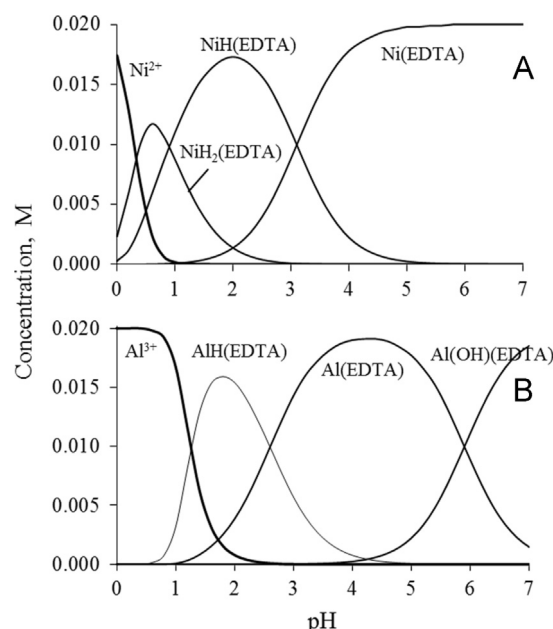


Fig. 3. Species distribution diagram of Ni (A) and Al (B), based on computer simulations, in an aqueous solution containing 0.1, 2×10^{-2} and 2×10^{-2} M of EDTA, Ni and Al, respectively.

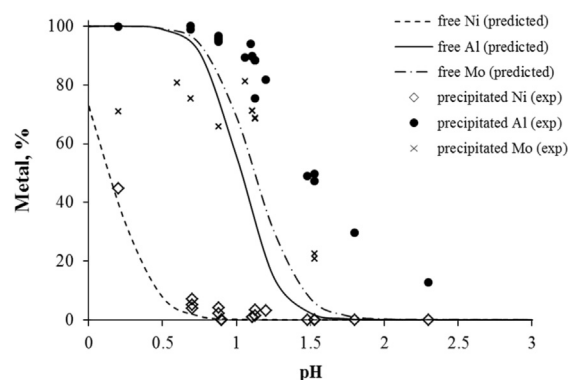


Fig. 4. Variation of Ni, Al and Mo precipitation at pH 5–6 after precipitation of EDTA at different pH (in x axis): comparison between predicted and experimental values. Each point represents a single experiment.

starts to dissociate, to form free Ni and free EDTA. So, when the pH of the first stage was below 0.5, more EDTA was recovered (Fig. 2), implying that, besides Al and Mo complexes, Ni–EDTA complexes were also partially broken. This fact was corroborated with the results obtained after increasing the pH (Fig. 4), where Ni precipitation was observed because it was already free of EDTA in some extent.

From the analysis of Fig. 4, we concluded that the pH of the first stage should be between 1.2 and 0.7 to guarantee a maximum precipitation of Al and Mo without any significant loss of Ni.

Fig. 5A shows the variation of Ni and Al precipitation with the pH of the second stage for three different pH values of the first stage. The pH of the second stage did not influence significantly the precipitation of Ni and Al.

Precipitation of Mo did not appear to be dependent of the pH of the first stage, as long as it was below 1.5 (Fig. 4). Below this pH, Mo–EDTA complexes start to break, leaving EDTA free to precipitate in the first stage and Mo when the pH was increased in the second stage. Mo precipitation does not go beyond 80% even when all Mo is predicted to be uncomplexed. This fact might be observed because at pH 5 Mo alone in solution is soluble, but since Al precipitates, Mo tends to co-precipitate, which was already observed (Pinto and Soares 2013b); so,

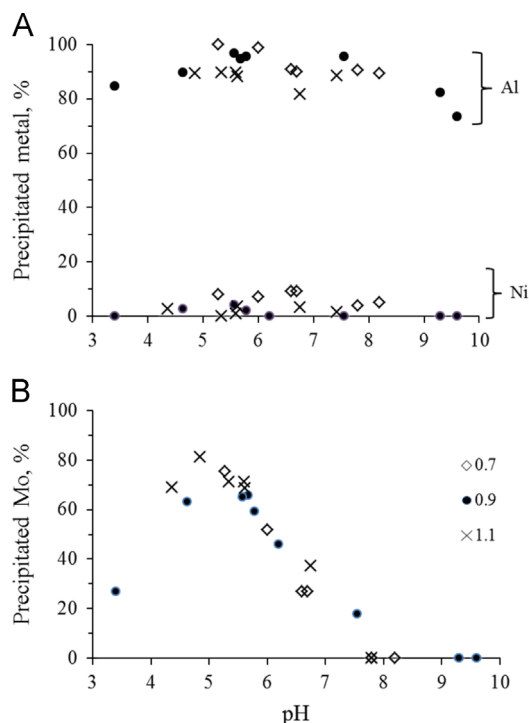


Fig. 5. Precipitation of Ni and Al (A) and Mo (B), at different pH values (in x axis) after precipitation of EDTA in acidic conditions (pH in figure legend). Each point represents a single experiment.

the amount of Mo precipitated is not dependent on the quantity of free metal ion. However, it was verified that the amount of Mo recovered varied with the pH of the second stage. Maximum values of precipitated Mo were reached between pH 4.5 and 5.5. As it can be seen in Fig. 5B, the tendency was very similar when different pH values of the first stage were compared. Analysis of variance (95% confidence level) corroborates that only the pH of the second stage has significant influence on the Mo precipitation, as long as the first stage occurred below pH 1.5.

These results showed that Al and Mo can be almost completely separated from Ni. After a stage at pH 0.9–1.0, $79 \pm 1\%$ of EDTA precipitated. Then, the pH was increased to 4–6, and $94 \pm 4\%$ of Al and $67 \pm 5\%$ of Mo precipitated with a loss of $3 \pm 1\%$ of Ni. The solid was mainly aluminum hydroxide, with a maximum of 4 wt% of Mo and 1.5 wt% of Ni. The solution obtained contained 1.13 g/L of Ni (1.92×10^{-2} M), 2.96×10^{-2} g/L of Al (1.10×10^{-3} M) and 3.82×10^{-2} g/L of Mo (3.96×10^{-4} M), as well as 0.020 M of EDTA. The mass ratios Ni/Al and Ni/Mo increased from 2.2 to 38 and from 10 to 30, respectively.

3.3. Recovery of nickel

The solution that resulted after the previous stage (Section 3.2) is mainly constituted by Ni and EDTA in a proportion of 1:1. At this ratio, Ni is complexed with EDTA in almost the whole pH range, which does not allow the recovery of Ni as a solid of nickel hydroxide by increasing the pH, due to the high stability of the Ni–EDTA complex.

In order to recover nickel, three different approaches, summarized in Fig. 1, were studied.

3.3.1. Option 1

As it was reported in Section 3.1, Ni–EDTA complexes are dissociated at pH below 0.5, which allowed an almost complete precipitation of EDTA. To facilitate the separation of Al from Ni,

discussed in Section 3.2, a higher pH was used in the precipitation of EDTA. After this step, the remaining EDTA could be separated by precipitation at a lower pH (< 0.5) so that Ni would be free to precipitate.

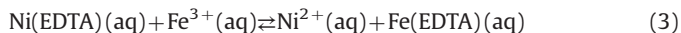
With this in mind, after the second stage, where Al and Mo were separated, pH values between 0 and 0.5 were tested. Because the concentration of EDTA was much smaller, dechelation kinetics was slower. Experiments were left for 3 days before separating the solid. After the addition of HNO_3 , no alteration was visible in the solution, but after 1 day, the formation of a solid was observed. Durations higher than 3 days did not affect the EDTA recovery. The best results were obtained between pH 0.2 and 0.4, where $70 \pm 3\%$ of EDTA was precipitated. The solid contain a maximum wt% of Ni of 0.02. By adding this result to the first EDTA precipitation at pH 0.9, the total recovery of EDTA was 86%. This value is slightly lower than the one obtained when the pH of the first stage was between 0.2 and 0.4 (94%). This is due to the decrease of the total concentration of EDTA and consequent modification of the equilibrium. After this stage, the remaining solution had 1.92×10^{-2} M of Ni and 5.9×10^{-3} M of EDTA.

Now, since most of the EDTA was precipitated and EDTA/Ni molar ratio was about 0.3, nickel was mostly present as free ion and could be precipitated, as $\text{Ni}(\text{OH})_2$, in alkaline medium. After addition of concentrated NaOH, it was verified that Ni precipitation reached 72%, even at pH up to 12. This result shows, as expected, that only free nickel precipitated while Ni–EDTA complexes remain unaltered in solution. The solid has a purity of 97%, with Al and Mo as the main impurities.

3.3.2. Option 2

Similarly to option 1, free EDTA was precipitated by decreasing the pH to 0.4, and the remaining EDTA stays complexed with Ni.

The replacement of Ni by another metal to allow a more complete precipitation and recovery of Ni was considered. Iron was chosen as it forms strong complexes with EDTA and is not toxic. In order to model the best pH conditions to replace Ni by Fe, computer simulations were performed considering $[\text{Ni}] = 2 \times 10^{-2}$ M and $[\text{EDTA}] = [\text{Fe}] = 6 \times 10^{-3}$ M. Fig. 6 shows that, below pH 3, EDTA complexes preferentially with Fe, leaving Ni free (Eq. (3)).



Above this pH, equilibrium starts favoring the Ni complexes, leaving Fe free to precipitate as iron hydroxide. Due to the excess of Ni, 70% are still free between pH 4 and 7, above this pH this fraction precipitates, which was observed experimentally (Section 3.3.1).

After Fe substitution, the precipitation of the free Ni cannot be achieved in the form of the hydroxide: the increase in the pH would lead to the dechelation and precipitation of Fe hydroxide that is more insoluble than the Ni one. Therefore, the hypothesis of recovering Ni, as a salt of nickel phosphate, which is more insoluble than the hydroxide, was studied. After the second precipitation step of EDTA (described in Section 3.3.1), Fe was added to the obtained solution and was left for a day in order to reach equilibrium. The blue Ni–EDTA solution transformed into a yellow solution containing Fe–EDTA. Then, phosphate ion was added in the form of Na_2HPO_4 solution.

3.3.2.1. Effect of the iron quantity. Iron is needed to replace Ni in the EDTA complexes; however, its amount cannot be in much excess compared to EDTA because it will precipitate together with Ni. Thus, $[\text{Fe}]/[\text{EDTA}]$ ratios between 1 and 1.3 were assayed for a reaction time of 2 min at pH=7 (Fig. 7A). It was concluded that the variation of the $[\text{Fe}]/[\text{EDTA}]$ ratio did not influence the recovery of Ni. This means that the replacement of Ni by Fe was complete and there is no need to add excess of Fe. Furthermore, Fig. 7A shows

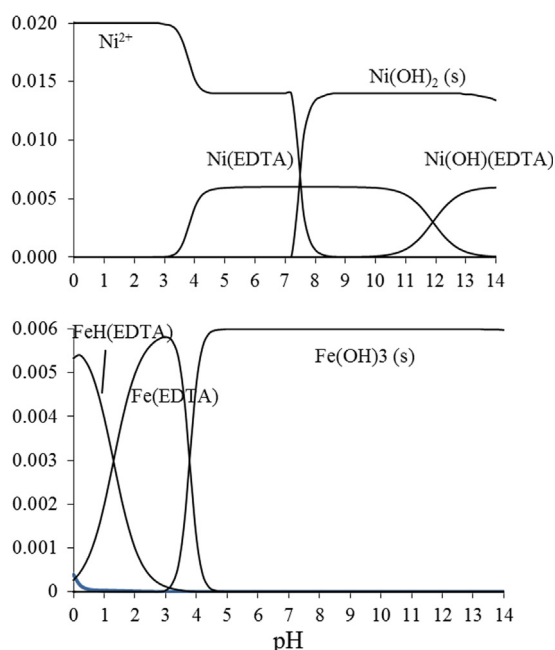


Fig. 6. Species distribution diagram of Ni (A) and Fe (B), based on computer simulations, in an aqueous solution containing $[\text{Ni}] = 2 \times 10^{-2} \text{ M}$ and $[\text{Fe}] = [\text{EDTA}] = 6 \times 10^{-3} \text{ M}$.

that the amount of Fe incorporated in the solid increases with the $[\text{Fe}]/[\text{EDTA}]$ ratio; so, a $[\text{Fe}]/[\text{EDTA}]$ ratio closer to 1, which is the stoichiometric quantity needed (Eq. (3)), is the best compromise between a high purity and high Ni recovery.

3.3.2.2. Effect of pH. It was verified that if the pH of Ni-EDTA solution was maintained ($\text{pH} = 0.4$), no precipitation of nickel phosphate occurred after the addition of the phosphate even though this addition increased the pH. Solubility of nickel phosphate decreases with the increase of the pH, with a minimum for pH between 9 and 10. So, after the addition of phosphate the pH was increased by adding NaOH. This was done after the addition of phosphate and not before: the pH of the Ni-Fe-EDTA solution cannot be increased to pH values higher than 2.5 otherwise EDTA starts to complex preferentially with Ni and Fe would immediately precipitate (Fig. 6), which was experimentally observed.

An increase in the Ni recovery with the pH was observed until pH 9 (Fig. 7B). Between pH 9 and 10, no meaningful changes have been detected. This behavior was consistent with the computer simulations where the minimum solubility of nickel phosphate is predicted between pH 9 and 10 (data not shown). Between pH 7.5 and 9.0, the precipitation of Ni increased almost 10%. The best Ni recovery results, $93 \pm 1\%$, were obtained at pH 9 after a reaction time of 2 min $[\text{PO}_4^{3-}]/[\text{Ni}^{2+}] = 1$ and $[\text{Fe}]/[\text{EDTA}] = 1$. In addition, the percentage of Fe in the solid increased continuously with the pH. This fact is well understood since higher pH favors the precipitation of $\text{Fe}(\text{OH})_3$ even in the presence of EDTA.

3.3.2.3. Effect of the phosphate quantity. In order to evaluate the suitable amount of phosphate needed to maximize the recovery of Ni, the molar ratio between phosphate and Ni was varied between 0 and 2.5. After the addition of the correspondent amount of phosphate, the pH was increased up to 9 with NaOH. The reaction was left to occur for 2 min and then the solid was separated by filtration. Fig. 7C shows the results obtained for different $[\text{PO}_4^{3-}]/[\text{Ni}^{2+}]$ ratios, both in terms of Ni recovery and percentage of Fe in

the solid. The goal is to recover Ni with the higher purity possible and not lose Fe to the solid. Without the addition of phosphate, both the recovery of Ni was lower and the percentage of Fe in the solid was higher due to the lower insolubility of nickel hydroxide. Between $[\text{PO}_4^{3-}]/[\text{Ni}^{2+}] = 0.7$ and 2.5 the differences in Ni precipitation were not significant. The quantities of Ni and P determined in the solid showed that the molar ratio between these two elements was always close to 1.5, indicating that the precipitated solid has a stoichiometry of $\text{Ni}_3(\text{PO}_4)_2$. In this case the minimum quantity of phosphate needed would be $[\text{PO}_4^{3-}]/[\text{Ni}^{2+}] = 0.667$, which explains the constancy of the results for ratios higher than 0.7. The percentages of Fe in the solid were also very similar between the experiments where $[\text{PO}_4^{3-}]/[\text{Ni}^{2+}]$ was between 0.7 and 2.5, although the tendency was decreasing with the increasing ratio.

3.3.2.4. Effect of reaction time. According to computer simulations, Fe would precipitate as $\text{Fe}(\text{PO}_4)_4$ to reach equilibrium, because Ni-EDTA complexes are stronger than Fe-EDTA complexes at this pH 9 (Fig. 6). Due to this reason, short reaction times (between 30 s and 20 min) were tested. The increase of Ni recovery was only significant between 30 s and 2 min; above this time, there were no statistical differences between results. The variance in the percentage of Fe present in the solid was also not significant between 2 and 20 min. From these results, a reaction time between 2 and 20 min can be used without compromising Ni recovery or purity.

3.3.3. Option 3

Based on the previous results, we decided to apply the Fe substitution as the third step of the process and remove the second EDTA precipitation step. The solution obtained after the second stage (separation of Al and Mo) has an equimolar concentration of Ni and EDTA (approximately $2 \times 10^{-2} \text{ M}$) and a pH between 5 and 6. Since the amount of Fe to be added should be equal to the EDTA present in solution (Eq. (3)), this implies that the quantity of Fe must be increased, when compared to the previous situation, and the pH must be lowered (< 2.5) to avoid iron precipitation. This option was studied in a similar way of what was already described in Section 3.3.2. The quantity of Fe was added to achieve a $[\text{Fe}]/[\text{EDTA}]$ ratio of 1. Higher quantities ($[\text{Fe}]/[\text{EDTA}] = 1.15$) were also tested but the percentage of Fe in the solid increased from 1 to 4%, as it happened previously (Fig. 7A). Similarly, reactions longer than 2 min and $[\text{PO}_4^{3-}]/[\text{Ni}^{2+}] \geq 0.7$ did not make significant differences in the Ni precipitation. The influence of pH was also studied, with the addition of NaOH after the addition of phosphates (Fig. 8). In this case, the increase of pH enhanced Ni precipitation, with a maximum Ni recovery of $82 \pm 2\%$ at pH 8.5. However, the amount of Fe, present in the precipitate, also increased more significantly with the pH than what was previously observed for the less concentrated EDTA solution (Fig. 7), due to the higher quantity of Fe added. To minimize the contamination of Fe ($< 2\%$), pH values lower than 8 should be used.

3.4. Proposal of a process to recover Ni from HDS spent catalysts

Fig. 1 summarizes the studies performed to recover Ni salts from spent catalysts. Leaching spent catalysts with an alkaline aqueous solution of EDTA, as the second leaching step of a process to recover metals from spent HDS catalysts, produces a solution of EDTA, Ni, Al and Mo (Pinto and Soares, 2013a). By lowering the pH to values close to 1, it is possible to recover the EDTA in excess relatively to Ni; this procedure leaves Al and Mo uncomplexed and able to precipitate at pH higher than 5. From this point, three options were studied to recover Ni.

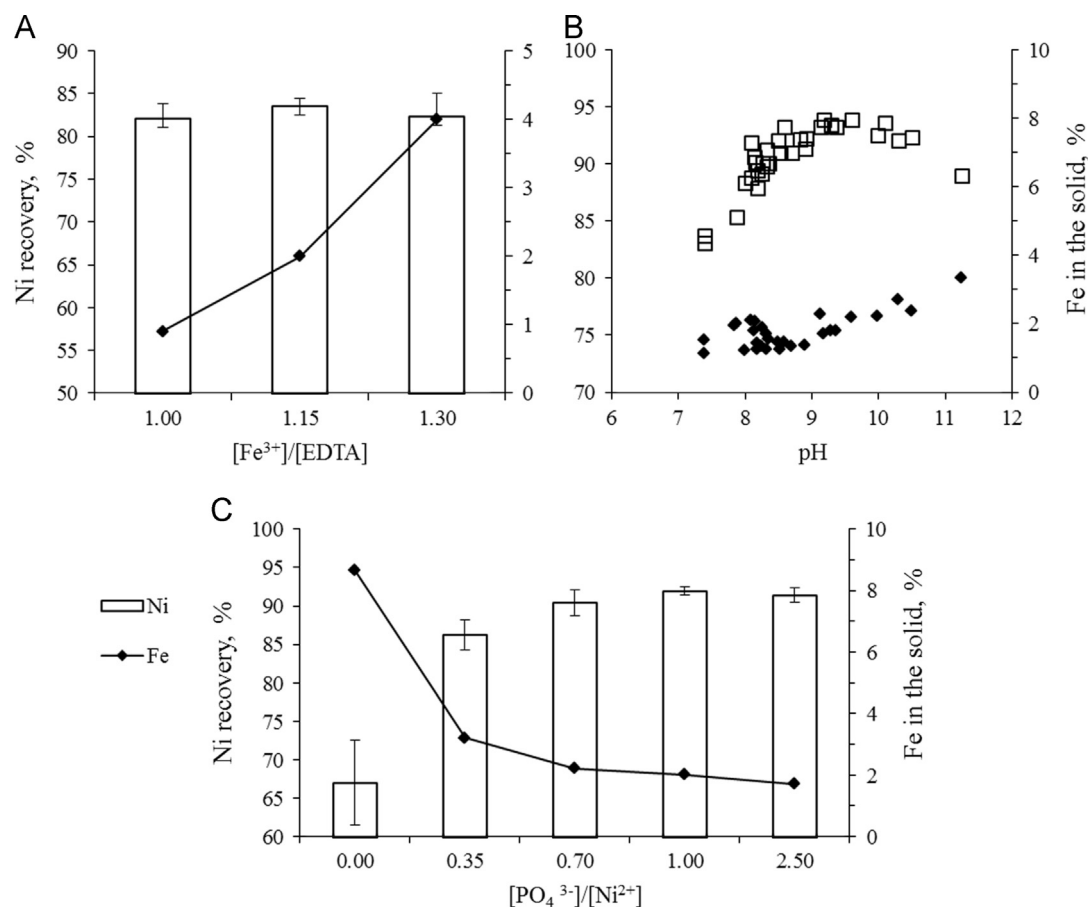


Fig. 7. Ni recovery, and respective percentage of Fe in the solid, obtained by substitution with Fe and precipitation with phosphate from an initial solution of $[Ni] = 1.9 \times 10^{-2}$ M and $[EDTA] = 5.9 \times 10^{-3}$ M. (A) Variation of $[Fe^{3+}]/[EDTA]$ molar ratio ($[PO_4^{3-}]/[Ni^{2+}] = 1$, $t = 2$ min, $pH = 7$, $n = 3$); (B) variation of pH ($[Fe]/[EDTA] = 1$, $[PO_4^{3-}]/[Ni^{2+}] = 1$, $t = 2$ min, each point represents a single experiment); (C) variation of $[PO_4^{3-}]/[Ni^{2+}]$ molar ratio ($[Fe]/[EDTA] = 1$, $t = 2$ min, $pH = 9$, $n = 3$).

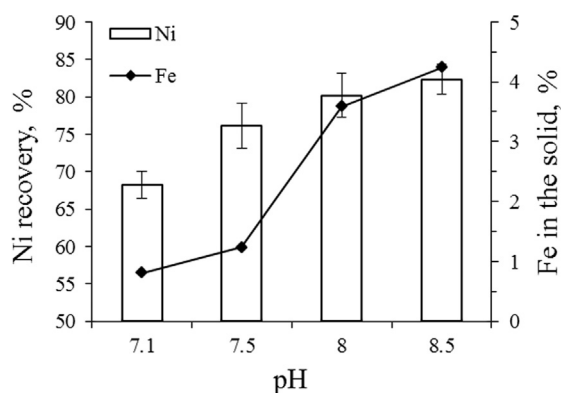


Fig. 8. Ni recovery (and respective percentage of Fe in the solid) obtained by substitution with Fe and precipitation with phosphate from an initial solution of $[Ni] = [EDTA] = 2 \times 10^{-2}$ M ($[Fe]/[EDTA] = 1$, $[PO_4^{3-}]/[Ni^{2+}] = 1$, $t = 2$ min, $n = 3$).

In option 1, EDTA was precipitated again, using a lower pH than the first EDTA precipitation step, in order to dissociate Ni–EDTA complexes. Then, free Ni can be precipitated, as nickel hydroxide, by increasing the pH.

Because extremely acidic conditions were not able to dissociate all Ni–EDTA complexes, the recovery of Ni was not complete. Therefore, two additional options (2 and 3) were developed for raising the yield of Ni recovery.

In option 2, we started by performing the second EDTA precipitation step. Then, in order to increase the amount of free

Ni, and thus the subsequent yield of nickel recovery, Fe was added for replacing Ni in the EDTA complexes and precipitation of Ni was achieved in the phosphate form. Similarly, option 3 was based on Fe replacement but directly after the Al and Mo precipitation step.

Finally, iron was separated and recovered as iron hydroxide from the solutions coming from options 2 and 3, by increasing the pH up to 12. To decrease costs, this iron hydroxide could be re-solubilized and added to the Ni–EDTA solution as the iron source.

A comparative analysis of the three options developed in this work for recovering Ni, shows that option 2 allows the higher Ni recovery. However, this option also includes a higher number of stages. Alternatively, option 3 has the advantage of using less amount of acid to lower the pH and does not include the slower stage that is EDTA second precipitation. Nevertheless, the quantity of Fe added was higher, which also decreased the purity of the recovered solid.

The processes proposed are nearly-closed with almost no generation of residues. The final solution obtained in option 2 contains around 6×10^{-3} mol/L EDTA and 3×10^{-3} mol/L of phosphate, less than 1.4×10^{-3} mol/L of Ni and 1.8×10^{-5} mol/L of Fe. In the case of option 3, EDTA, phosphate and Ni concentrations are about two to three times higher. The effluent coming from option 1 can be reused again in the leaching stage of the spent catalyst, after correcting the EDTA concentration with the recovered and some fresh EDTA, with a purge to avoid the accumulation of contaminants, or appropriately treated and disposed. In option 1, the final solution contains Ni and EDTA at a proportion of 1:1 and concentration of about 6×10^{-3} mol/L.

Table 2Comparison between the three proposed options, in terms of reagents consumptions and costs, to treat 1 m³ of solution.

Reagent	Price ^a (USD/kg)	Consumption (kg)			Cost (USD)		
		Option 1	Option 2	Option3	Option 1	Option 2	Option 3
HCl, 33%	0.15	55.0	55.0	12.2	8.25	8.25	1.82
NaOH	0.40	20.0	19.4	19.4	8.00	7.77	7.77
FeCl ₃ · 6H ₂ O	0.35	–	1.6	5.4		0.57	1.89
Na ₂ HPO ₄ · 12H ₂ O	1.1	–	5.0	5.0		5.52	5.52
Total					16.25	22.11	17.00

^a Based on several industrial suppliers and ICIS Indicative Chemical Prices.

The final solid of nickel phosphate can be used in electroplating processes as a source of both Ni and P (Matsushima, 1978). Nickel phosphate is also useful in cathode electrodes (Lee et al., 2011), catalysts (Samadi-Maybodi, 2011) and as an inorganic pigment (Onoda et al., 2007). Nickel hydroxide is usually applied in electro-chemical cells and batteries or used as an intermediate to produce catalysts and nickel powder.

All the proposed processes were based on precipitation operations that occur at room temperature; this is an important advantage when thinking in the scale-up of the process because it is based on simple and economic viable unit operations. On the other hand, the main difficulty might be the control of the optimal amount of Fe addition to maximize Ni recovery and avoid excessive contamination of the solid, which requires control of the EDTA concentration in solution.

Since the metal products are recovered from an industrial residue, most of the costs are due to acid, base, iron and phosphate consumption. Table 2 shows a comparison of the reagent costs for the three options. Hydrochloric acid was chosen to decrease the pH instead of nitric due to its lower cost. This is only an estimation based on the average prices at industrial scale and should not be considered as an extensive economical evaluation. Also, these calculations do not include the possible reutilization of iron. Option 2 is the most expensive due to the larger consumption of reagents but it is also the one with greater recovery of Ni and with fewer impurities when compared to option 3. For that reason, the final product is more valuable; however, it is difficult to predict the actual price of each product, which unables the overall evaluation of the return associated with each option proposed.

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